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An Intercomparison of Measurement Systems for Vapor and Particulate Phase Concentrations of Formic and Acetic Acids

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During June 1986, eight systems for measuring vapor phase and four for measuring particulate phase concentrations of formic acid (HCOOH) and acetic acid (CH_3COOH) were intercompared in central Virginia. HCOOH and CH_3COOH vapors were sampled by condensate, mist, Chromosorb 103 GC resin, NaOH-coated annular denuders, NaOH impregnated quartz filters, K_2CO_3 and Na_2CO_3 impregnated cellulose filters, and Nylasorb membranes. Atmospheric aerosol was collected on Teflon and Nuclepore filters using both hi-vol and lo-vol systems to measure particulate phase concentrations. Samples were collected during 31 discrete day and night intervals of 0.5–2 hour duration over a 4-day period. Performance of the mist chamber and K_2CO_3 impregnated filter techniques were also evaluated using zero air and ambient air spiked with $HCOOH_g$, CH_3COOH_g, and formaldehyde (CH_2O_g) from permeation sources. Results of this intercomparison show significant systematic and episodic artifacts among many currently deployed measurement systems for $HCOOH_g$ and CH_3COOH_g. The spiking experiments revealed no significant interferences for the mist chamber technique and results generated by the mist chamber and denuder techniques were statistically indistinguishable. The condensate technique showed general agreement with the mist chamber and denuder methods, but episodic bias between these systems was inferred from large and significant differences observed during the first day of sampling. Nylasorb membranes are unacceptable for collecting carboxylic acid vapors as they did not retain $HCOOH_g$ and CH_3COOH_g quantitatively. Strong base impregnated filter and GC resin sampling techniques are prone to large positive interferences apparently resulting, in part, from reactions involving CH_2O_g to generate HCOOH and CH_3COOH subsequent to collection. Significant bias presumably associated with differences in postcollection handling was observed for particulate phase measurements by participating groups. Analytical bias did not contribute significantly to differences in vapor and particulate phase measurements.

INTRODUCTION

Formic acid (HCOOH) and acetic acid (CH_3COOH) are major chemical constituents of precipitation [e.g., *Keene and Galloway*, 1986] and cloud water [e.g., *Weathers et al.*, 1988]. Relative to the large data bases of aqueous phase observations, however, few measurements of these acids in the vapor and particulate phase have been reported [e.g., *Andreae et al.*, 1988; *Dawson and Farmer*, 1988; *Talbot et al.*, 1988]. Theoretical considerations suggest that HCOOH and CH_3COOH may be involved in potentially important atmospheric chemical transformation sequences [e.g., *Chameides and Davis*, 1983; *Jacob*, 1986; *Jacob and Wofsy*, 1988], and this realization has stimulated investigators to initiate multiphase sampling for these constituents. A variety of measurement techniques for determining vapor and particulate phase concentrations of HCOOH and CH_3COOH are currently in use, but few have been rigorously tested to assess potential artifacts associated with sampling and analysis. Intercomparing field measurements of atmospheric constituents obtained at a common place and time, but using different types of measurement systems has proved to be a valuable tool for identifying such artifacts [e.g., *Hoell et al.*, 1985; *Mulawa and Cadle*, 1985; *Anlauf et al.*, 1985; *Fehsenfeld et al.*, 1987]. Between June 10, and June 13, 1986, a number of investigators from seven different research groups gathered in Charlottesville, Virginia, and intercompared eight measurement techniques for vapor phase and four particulate phase concentrations of HCOOH and CH_3COOH. This paper reports the results of that intercomparison.

METHODS

Sampling and Analytical Systems

The methods of collection, conditions of sample storage, extraction procedures and analytical techniques for measurement systems of participating groups are summarized in

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Tables 1 and 2. Vapor phase species were sampled by 8 different techniques. Washington State University (WSU) collected soluble gases using the condensate technique as described by *Farmer and Dawson* [1982]. The University of Virginia (UVA) operated two collection systems for vapor. UVA 1 modified a technique described by *Haynes* [1979] to remove carboxylic acids from an airstream pulled through Chromosorb 103 GC resin packed in 4.76 mm ID Tygon columns. UVA 2 collected vapor on two tandem Nylon membranes mounted on separate stages of polycarbonate cassettes. Peaks for carboxylic acids had been observed previously during ion chromatograph analysis of extracts from Nylon membranes used to collect HNO_3 vapor. In response to this observation, it was decided to include the UVA 2 system in the intercomparison, despite the fact that its performance in terms of specificity or collection efficiency had not been previously tested. Florida State University (FSU) collected acidic gases from an air stream pulled through 25 mm cellulose paper filters which were impregnated with 1.8 M K_2CO_3 and mounted in polycarbonate cassettes. The California Institute of Technology (CIT) operated a similar system consisting of 47 mm quartz fiber filters which were impregnated with 0.025 M NaOH and mounted in polycarbonate cassettes. The NOAA Aeronomy Laboratory (NOAA) collected acidic gases on 90 mm cellulose paper filters which were impregnated with 0.02 M Na_2CO_3 and mounted in polycarbonate cassettes. The NASA Langley Research Center (NASA) collected water-soluble trace gases with a mist chamber as described by *Cofer et al.* [1985] and *Talbot et al.* [1988]. The Technical University of Vienna (TUW) collected acidic vapor using annular denuder tubes coated with 0.10 M NaOH as described by *Rosenberg et al.* [1988]. With the exception of the WSU's condensate sampler and TUW's denuder tubes, both of which exclude particles by the nature of collection, all of the above systems incorporated upstream prefilters to remove particles from the air stream prior to collection of vapor phase carboxylic acids.

Data from four measurement systems for particulate phase carboxylic acids were also intercompared. Because of short sampling times (~1 hour), low sampling rates (Table 1), and low ambient concentrations (see Results and Discussion), little particulate material was deposited on the upstream filters of the previously described samplers for vapor, and consequently most of these systems had inadequate resolution for quantifying particulate phase concentrations. Only NOAA generated enough observations above system detection limits to statistically compare with results from the hi-vol sampling systems for particles operated by UVA 1 and NASA. The two hi-vol systems collected particles on 102 mm, 2.0 μm Teflon (Zefluor) filters mounted in open face stainless steel housings. In addition to the above three systems, NASA operated a low-vol sampling system for particles consisting of stacked 47 mm filters mounted in polycarbonate cassettes. The front filter for coarse particles was an 8.0 μm Nuclepore filter followed by a 2.0-μm Teflon (Zefluor) filter for fine particles. The aerodynamic cutoff diameter between the two particle fractions was 1.5 μm [*John et al.*, 1983]. To obtain sufficient sample for analysis, this system was operated for time periods ranging from 2 to 6 hours.

The performance of each analytical laboratory was intercompared with blind audit solutions which bracketed the typical concentration ranges for intercomparison samples. These solutions were prepared by UVA, treated with $CHCl_3$ to prevent microbial transformation [*Keene et al.*, 1983], and distributed to each group during the intercomparison.

Mean detection limits (Table 3) were estimated from the combined uncertainties associated with samples, field blanks, and sampling rates, following in part the procedures recommended by *Currie* [1968]. These estimates are based on the assumption that the standard error is approximately constant for each system in the range between 0 and the calculated detection limit. We further assume that the standard deviation for samples (S_S) at the detection limit is approximately equal to the standard deviation for replicate field blanks (S_B) run during the course of the intercomparison. The overall uncertainties (S_0) associated with samples and blanks can be combined as follows:

$$S_0 = (S_S^2 + S_B^2)^{1/2}$$

but

$$S_S = S_B$$

so

$$S_0 = (2S_B^2)^{1/2}$$

Uncertainties in sampling rates (U_R) were estimated in units of percent from calibration or from manufacturer's specifications. At the detection limit, this uncertainty can be approximated in units of nmol by

$$S_V = U_R S_0$$

The mean detection limit (MDL) at 95% confidence can then be expressed as

$$\text{MDL} = 1.96 * \frac{(S_0^2 + S_V^2)^{1/2}}{V_S}$$

where V_S is the mean sample volume.

We recognize that the procedure for including flow uncertainties in overall uncertainties represents an approximation and is not a rigorous statistical formulation. We believe, however, that this approach does represent a reasonable quantitative estimate of the detection limit.

Experimental Design

Sampling apparatus were operated on the southeastern roof of the Environmental Sciences Building (Clark Hall) at the University of Virginia in Charlottesville, Virginia, between June 10, and June 13, 1986. Inlets were positioned at a height of 1–1.5 m above the roof surface (20 m above ground level) at the locations indicated on Figure 1. Exhaust from the pumps was collected in a common manifold and discharged on the opposite (northwest) side of the building approximately 60 m distance and 20 m below the sample inlets. Samples were collected simultaneously during 31 discrete intervals ranging from 0.5 to 2 hours in duration. The TUW denuder system required somewhat longer sampling times for adequate resolution, and therefore their samples were collected over longer time intervals (2 hours) relative to most other systems (typically 1 hour). To ensure that the same air parcels were sampled, air flow through the denuder tubes was stopped when the other systems were shut off for servicing. To minimize possible effects of phase

TABLE 1. Collection Systems and Sample Storage

Principal Investigator	Organization	Code	Collection of Particles	Collection of Vapor	Mean Sampling Rate (SLPM)	Sample Storage Prior to Analysis
Carl Farmer	Washington State University	WSU	not collected	Condensate [*Farmer and Dawson*, 1982]	10–20	Vapor: condensate was treated with 5 mL $CHCl_3$ and refrigerated in glass vial at 5°C.
William Keene	University of Virginia	UVA 1	102 mm Teflon filters (2.0 μm Zefluor)	50 mg 20–40 mesh Chromosorb^R 103 GC resin [*Haynes*, 1979] packed in 4.76 mm ID Tygon columns. Particles were removed with an upstream 47 mm Teflon filter (2.0 μm Zefluor).	particles, 580. vapor, 10.5	Particles: filters were removed from holders, placed in glass vials, and frozen at −4°C. Vapor: cartridges were stored in 2 polyethylene bags and frozen at −4°C.
Meinrat Andreae	Florida State University	FSU	not analyzed	25 mm cellulose filters (Schleicher and Schuell) impregnated with 1.8 M K_2CO_3 in 10% glycerol:H_2O solution. Particles were removed with an upstream 47 mm Teflon filter (2.0 μm Zefluor).	20.	Vapor: filters were extracted, treated with 100 μL $CHCl_3$, and analyzed immediately.
William Munger	California Institute of Technology	CIT	not analyzed	47 mm quartz filters (Whatman QMA) impregnated with 1 mL of 0.025 M NaOH in ethanol. Particles were removed with an upstream 47 mm Teflon filter (1.0 μm Zefluor).	10.6	Vapor: filters were removed from holders, placed in plastic petri dishes, and frozen at −4°C.
Richard Norton	Aeronomy Laboratory	NOAA	90 mm Teflon filters (1.0 μm Zefluor)	90 mm cellulose (Whatman 41) impregnated with 0.02 M Na_2CO_3 in 10% glycerol:H_2O solution	85.	Filters were removed from holders, placed in polyethylene bags, and refrigerated at 4°C.
Alexander Pszenny	University of Virginia	UVA 2	47 mm Teflon filters (2.0 μm Zefluor)	Tandem 47 mm Nylon membranes (Nylasorb)	52.5	Filters were removed from holders, placed in plastic petri dishes, stored in 2 polyethylene bags, and frozen at −4°C.
Robert Talbot	Langley Research Center	NASA	47 mm Nuclepore filters (8.0 μm); 47 mm Teflon filters (2.0 μm Zefluor); 102 mm Teflon filters (2.0 μm (Zefluor)	Mist chamber [Cofer et al., 1985]. Particles were removed with an upstream 47 mm Teflon filter (2.0 μm Zefluor)	particles (stacked), 20. particles (hi-vol), 580. vapor, 7.	Particles: filters were removed from holders, placed in a polyethylene bag, and stored in dark at room temperature. Vapor: solution was treated with 50 μL $CHCl_3$ and analyzed immediately.
Wilfried Winiwarter	Technical University of Wien (Vienna)	TUW	not analyzed	Two anular denuders (in series) each coated with 4 mL of 0.10 M NaOH in 90% methanol	10.	Vapor: HCOOH in untreated eluent was measured immediately after collection. CH_3COOH was measured within 2 weeks in eluent treated with 50 μL $CHCl_3$ and refrigerated at 4°C.

TABLE 2. Analytical Systems

Group	Extraction Procedure		Sample Pretreatment/Matrix Matching		Analytical Technique	Column Type and Manufacturer			Eluent	Injection Volume, μL
	Particles	Vapor	Particles	Vapor		Guard	Separator	Suppressor		
WSU	not collected	none	not collected	none	I.C.	HPIC-AG4A (Dionex)	HPIC-AS4A (Dionex)	AMMS (Dionex)	1.0 mM $Na_2B_4O_7$	250
UVA 1	wetted with 1 mL of methanol and extracted for 10 min in 10 mL of eluent under sonication	Extracted for 20 min in 10 mL of H_2O and filtered (Whatman 41)	Methanol added to eluent to match sample matrix	HCl added to sample to match eluent matrix	I.C.E.	none	HPICE-ASI (Dionex)	ISC (Dionex)	1.0 mM HCl	500
FSU	not analyzed	extracted for >15 min in 5 mL of H_2O while shaking	not analyzed	none	I.C.E.	none	HPICE-ASI (Dionex)	ISC (Dionex)	1.0 mM HCl	50
CIT	not analyzed	extracted for >1 hour in 10 mL of H_2O in reciprocating shaker	not analyzed	none	I.C.	HPIC-AG4A (Dionex)	HPIC-AS4A (Dionex)	AMMS (Dionex)	4.0 mM $Na_2B_4O_7$	50
NOAA	extracted for 15 min in 10 mL of eluent under sonication and stored in refrigerator over night	extracted for 15 min in 10 mL of eluent under sonication and stored in refrigerator over night	none	none	I.C.	HPIC-AG4 (Dionex)	HPIC-AS4 (Dionex)	AMMS (Dionex)	1.0 mM $Na_2B_4O_7$	250
UVA 2	wetted with 0.3 mL methanol and desorbed for 30 min in 10 mL of H_2O under sonication	desorbed for 30 min in 10 mL of eluent (containing 0.3% H_2O_2) under sonication	none	none	I.C.	HPIC-AG3 (Dionex)	HPIC-AS3 (Dionex)	AFS-1 (Dionex)	0.75 mM $NaHCO_3$	500
NASA	Nuclepore extracted twice for 15 min each with 5 mL of H_2O; 47 mm Teflon wetted with 0.4 mL of methanol and extracted twice for 15 min each with 5 mL of H_2O; 102 mm Teflon wetted with 1.0 mL of methanol and extracted 3 times for 15 min each with 5 mL of H_2O. All extracts treated with 50 μL of $CHCl_3$ after bulking.	none	$CHCl_3$ added to standard solutions to match sample matrix	$CHCl_3$ added to standard solutions to match sample matrix	I.C.	HPIC-AG4A (Dionex)	HPIC-AS4A (Dionex)	AMMS (Dionex)	0.5 mM $NaCO_3$	500

TABLE 2. (continued)

Group	Extraction Procedure		Sample Pretreatment/Matrix Matching		Analytical Technique	Column Type and Manufacturer				Eluent	Injection Volume, μL
	Particles	Vapor	Particles	Vapor		Guard	Separator	Suppressor			
TUW	not analyzed	eluted for 2 min in 3 mL of H_2O	not analyzed	none	$HCOO_T$ I.C.	HPIC-AG3 (Dionex)	HPIC-AS3 (Dionex)	AFS-1 (Dionex)		0.75 mM $NaHCO_3$	500
					CH_3COO_T I.C.E.	none	ICN (Wescan)	none		0.25 mM H_2SO_4	100

change as material accumulated on the particle filters, the hi-vol samplers were typically run for only the middle 30 min interval of each 1 hour sampling period.

Statistical Evaluations

Both parametric and nonparametric statistics were used to test the significance of differences between results generated by the various measurement systems. The Non-Parametric Median Test was employed to assess the null hypothesis that the independent distributions for all data sets are from populations with the same median. The Kruskas-Wallis nonparametric alternative to 1-way ANOVA tested the null hypothesis that the distributions for all data sets represent random samples from identical populations. Each data set was then compared with every other data set. The Mann-Whitney technique was applied to test the null hypothesis that each paired data set had the same distribution. The reduced major axis (RMA) procedure was subsequently used to calculate slopes and intercepts for linear regressions between each paired data set. Positive or negative artifacts were inferred if slopes or intercepts of the regressions differed significantly from 1 and 0, respectively. *Keene et al.* [1986] assessed the assumptions and justified the use of this technique for testing hypotheses involving the chemical composition of atmospheric samples.

Postintercomparison Experiments

FSU and NASA performed two sets of additional experiments to identify the nature of the bias between their respective measurement systems for vapor phase species (see Results and Discussion section). The first three experiments were performed at the FSU campus in Tallahassee, Florida, on November 3–4, 1986. At the time of the experiments, the flow meters and analytical systems for the two systems were intercompared to assess any bias that might be attributable to these sources. Flow measurements agreed within 1% and analytical results within 3%.

Experiment 1. HCOOH and CH_3COOH vapor was generated by permeation cells, diluted with zero air using a Metronics Dynacalibrator 340, and delivered to a Teflon manifold where the vapor was sampled simultaneously by the two systems. Data for the long-term weight loss from the permeation cells was not available at the time of the experiment, and therefore an estimate of the concentrations of vapor species in the calibration gas stream was not obtained independent of the chemical measurements.

Experiment 2. The two systems were positioned on the roof of the Oceanography Building at FSU and simultaneously sampled ambient air for two consecutive intervals of 1 and 2 hours each.

Experiment 3. Ambient air was sampled simultaneously by two separate FSU impregnated filters. One filter sampled only ambient air while the second filter sampled ambient air with CH_2O added via a permeation source to produce a gas phase concentration in the range of 400–600 nmol/SCM (approximately 10–15 parts per billion by volume). The concentrations of CH_2O in the air stream were high relative to many ambient levels reported in the literature (for example, see *Duce et al.* [1983] and *Puxbaum et al.* [1988]), and any related artifacts are expected to approach upper limits.

A second set of experiments was performed at the NASA Langley Research Center in Hampton, Virginia on November 10–11, 1986. Prior to the experiments, CH_2O vapor was

TABLE 3. Mean Detection Limits (nmol/SCM for 1 Hour Sample)

	Vapor		Particulate	
Group	HCOOH	CH_3COOH	HCOOH	CH_3COOH
WSU*	0.8	0.7	NA	NA
UVA 1	35.5	···	1.3	0.6
FSU	9.7	2.6	3.8	1.9 (coarse)
			1.1	2.0 (fine)
CIT	247.	421.	ND	ND
NOAA	0.37	NR	0.041	NR
UVA 2	NR	NR	2.5	4.8
NASA	0.88	1.9	0.17	0.22 (coarse)
			0.11	0.19 (fine)
			0.30	0.31 (hi-vol)
TUW†	2.7	16.1	NA	NA

NA, not applicable; ND, not determined; and NR, not reported because technique was not qualitative (see Results and Discussion). Three center dots indicate high background on the resin prevented quantification of CH_3COOH_g during the short sampling periods of the intercomparison.

*Corresponds to mean dew point and temperature during intercomparison (these limits are achievable in a sampling time of approximately 10–15 min).

†Based on 2-hour sampling time.

generated by a permeation cell and supplied to a Teflon sampling manifold. The vapor phase concentration of CH_2O in the sampled air was approximately 500 nmol/SCM based on data for long-term weight loss from the cell. Background levels of HCOOH and CH_3COOH in the zero air stream to which CH_2O had been added were then determined by sampling the streams with each system. Concentrations of both acids measured by FSU were below the detection limits (Table 3). For the mist chamber, CH_3COOH was below the detection limit (Table 3), but HCOOH was found at a concentration of 3.3 ± 0.2 nmol/SCM (N = 4).

Experiment 4. Ambient air was sampled simultaneously by two mist chambers. One chamber sampled only ambient air, while a second sampled ambient air with CH_2O added via a permeation source to produce a concentration of approximately 400 nmol/SCM.

Experiment 5. Ambient air was sampled simultaneously by two pairs of impregnated filters. One set sampled only ambient air, while the second sampled ambient air with CH_2O added at the same level as in experiment 4. Unspiked ambient air was also sampled with the mist chamber during the collection period.

Experiment 6. A final experiment was conducted to assess the effects of different storage procedures for aerosol samples. Duplicate samples were collected on Teflon filters that were then cut in half. One half of each filter was sealed separately in double polyethylene bags and stored in the dark at 4°C. Each remaining filter half was placed in a

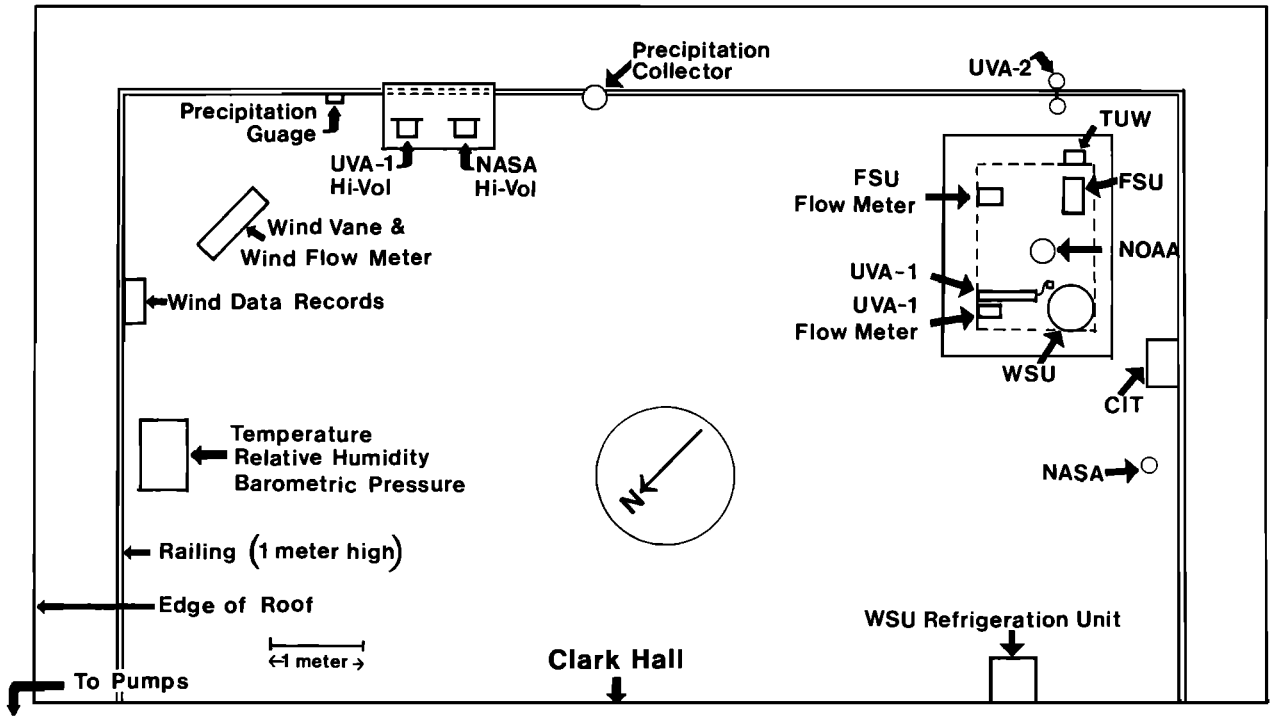

Fig. 1. Arrangement of sampling equipment during the intercomparison.

TABLE 4. Mean Meteorological Conditions During Each Sampling Interval

Date	Time EDST	Temperature, °C	Dew Point, °C	Barometric Pressure, mbar	Wind Speed, m/s	Wind Direction
June 10, 1986	1121–1221	25.7	13.7	1024.	NA	S
	1226–1326	27.3	14.7	1023.	NA	SW
	1332–1432	28.2	14.8	1023.	0.6	SW
	1437–1537	28.2	14.6	1022.	<0.5	SW
	1543–1643	28.1	15.4	1021.	<0.5	S
	1647–1747	26.5	15.4	1021.	<0.5	S
June 11, 1986	0807–0907	23.0	17.9	1015.	<0.5	S
	0917–1017*	24.4	18.8	1015.	<0.5	S
	1023–1123	25.9	19.8	1015.	<0.5	SW
	1128–1228	28.1	20.6	1015.	0.6	S
	1233–1333	29.2	21.0	1015.	<0.5	S
	1337–1437	31.3	21.1	1015.	<0.5	SW
	1442–1542	32.9	20.8	1014.	<0.5	S
	1547–1647	33.4	20.9	1012.	<0.5	S
	1652–1752†	31.5	21.9	1011.	<0.5	S
	1757–1857	29.2	23.5	1011.	<0.5	S
	1903–2003	28.8	22.5	1011.	0.6	SW
	2009–2019	28.0	22.1	1011.	<0.5	SW
	2115–2215	26.8	22.1	1012.	<0.5	SW
	2222–2322	26.1	21.5	1012.	<0.5	S
June 12, 1986	0031–0231	23.9	21.2	1012.	<0.5	S
	0300–0500	22.8	21.2	1011.	<0.5	S
	1237–1337	32.8	19.7	1011.	NA	NA
	1341–1442	33.5	19.7	1011.	NA	NA
	1446–1546	33.1	19.1	1010.	NA	S
	1550–1650	33.5	18.9	1009.	NA	variable
	1654–1754	33.5	11.8	1009.	NA	S
June 13, 1986	0804–0904	25.7	15.6	1017.	<0.5	variable
	0909–1009	27.7	15.2	1017.	<0.5	S
	1015–1115	28.8	14.9	1017.	<0.5	SE
	1121–1221	30.0	15.0	1018.	<0.5	SW

NA, not available.
*Trace amount of rain fell between 0750 and 0955.
†0.05 cm of rain fell between 1730 and 1741.

separate Teflon centrifuge tube, sealed in a polyethylene bag, and stored in the dark at −5°C. Filters were stored for a period of 20 days prior to analysis. A second set of duplicate filters was collected during a different period of time, halved, and analyzed within 2 hours of collection. Results from these analyses were used to assess the variation between filter halves resulting from nonhomogeneity of blanks and samples.

Results and Discussion

Meteorological Conditions

Meteorological conditions during the course of the intercomparison can be characterized as warm and humid with light and variable winds (Table 4). Wind speed and direction measured on the roof of Clark Hall were undoubtedly affected by the building's geometry and are not expected to be representative of surface winds in the region.

During the first day of the intercomparison (June 10), weather was dominated by a large high pressure system centered over Pennsylvania. Surface winds were predominately from the east. This system moved off shore overnight as a warm front approached Charlottesville from the west. By the morning of June 11, surface winds shifted and were now blowing from the south. The front stalled and weakened when it reached the mountains to the west of town and by midnight ceased to be an identifiable feature. Two light rain showers fell during the sampling on June 11 (Table 4). A low pressure system centered over Illinois strengthened during the morning of June 12 and began moving in an easterly direction. Surface winds shifted to the southwest as a trailing cold front from the low approached the region. By the morning of June 13, a weak depression had formed over Maryland, but surface winds were still out of the southwest. The front passed through Charlottesville at approximately 0800 hours on the morning of June 13 with an associated shift in surface winds to out of the west.

Vapor Phase Species

The concentrations of formic acid vapor ($HCOOH_g$) and acetic acid vapor (CH_3COOH_g) measured by participating groups during the intercomparison are shown in Figures 2 and 3, respectively. Results for all systems during the 20 hours sampling on June 11–12 indicate marked diel cycles for both species with rising concentrations during the day and falling concentrations at night. Similar cycles have been observed at Hampton, Virginia [*Talbot et al.*, 1988] and in the Amazonian region of Brazil [*Andreae et al.*, 1988]. Despite these general similarities, large differences existed in concentrations measured with the various techniques.

Results obtained by UVA-2 indicate that Nylasorb membranes do not retain $HCOOH_g$ or CH_3COOH_g quantitatively. Higher concentrations of both acid species were consistently found on the second of the tandem membranes, suggesting that one or more other species in the air streams either competes for collection sites or reacts with and

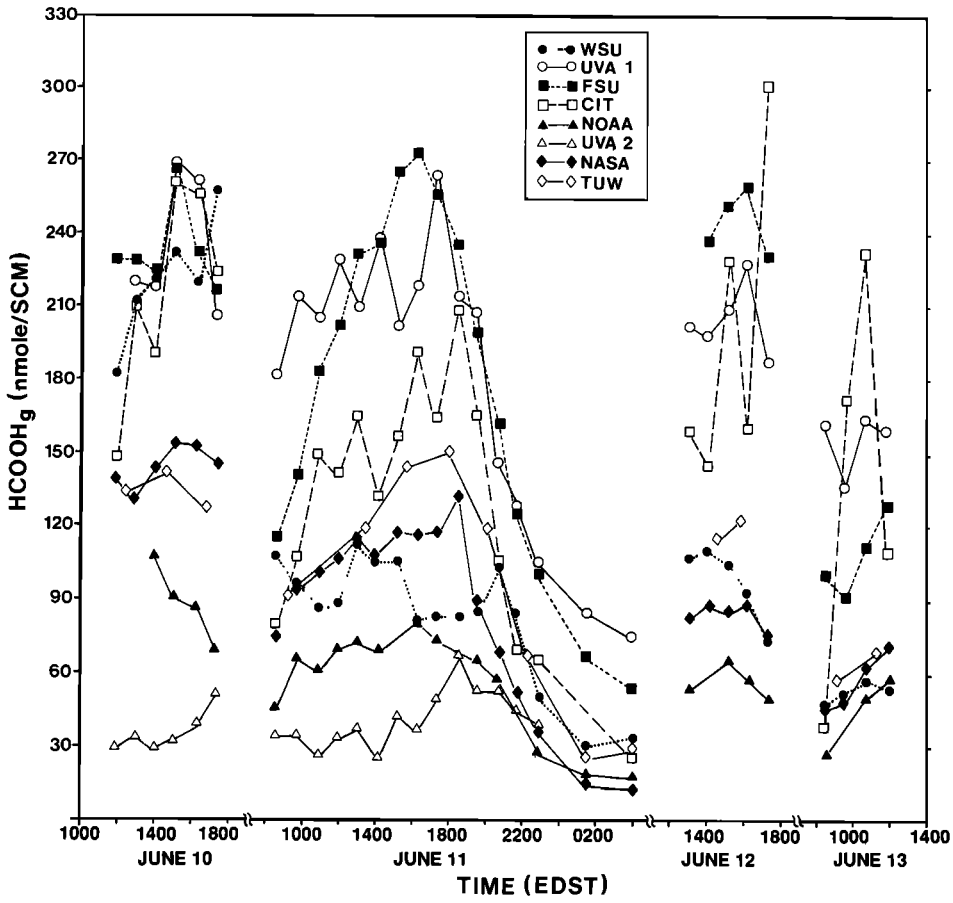

Fig. 2. Concentrations of $HCOOH_g$ measured during the intercomparison.

destroys part of the $HCOOH_g$ and CH_3COOH_g sorbed onto the membranes. Later field tests with a Teflon/Nylon pair situated as a prefilter for a mist chamber sampler have shown that Nylasorb membranes have poor collection efficiency for vapor phase HCOOH and CH_3COOH (R. W. Talbot, personal communication, 1988). Results generated using Nylon membranes were therefore dropped from further evaluation.

Formic acid intercomparison. The null hypotheses that the independent distributions for all data sets were from populations with the same median and that the distributions for all data sets represent random samples from identical populations were rejected at 95% confidence. These results indicate that significant bias exists among concentrations measured by the seven remaining techniques.

Results of hypothesis tests involving the Mann-Whitney technique and the RMA procedure are summarized in Figure 4. No significant differences between results for NASA and TUW were detected. Relative to UVA 1, FSU, and CIT, however, systematic and generally significant differences in slope parameters suggest that NASA and TUW measured consistently lower concentrations of $HCOOH_g$. Systematic positive or negative artifacts can be inferred from the results between these two groups of measurement systems.

The significant differences in the slope and intercept for results generated by WSU and NASA resulted in part from significantly different concentrations of $HCOOH_g$ measured by the two systems during the six sampling periods on June 10 (Figure 2). NASA and TUW measured similar concentrations during this period. Differences between WSU, NASA, and TUW during the remainder of the intercomparison were not significant. These observations suggest that WSU or NASA and TUW may experience episodic artifacts relative to one another.

The regressions of results for UVA 1 with most other systems exhibit significant positive or negative intercepts (Figure 4) resulting in part from the high concentrations of $HCOOH_g$ measured by UVA 1 during the 4 sampling intervals on June 13. When these four measurements were removed, there were no significant differences between results for UVA 1 and FSU, and intercepts for regressions with most other systems were not significantly different from 0. These observations suggest that the UVA 1 system may also experience episodic artifacts.

The generally low correlation coefficients for regressions of CIT results with other systems result from large variability in their field blanks. Hypothesis tests involving the distributions and the regression slope and intercept with FSU results indicate no significant differences in the 2 data sets.

NOAA measured significantly lower concentrations of $HCOOH_g$ relative to most other systems (Figures 2 and 4). Independent testing using tandem filter assemblies indicates that these differences were not associated with collection inefficiencies. We infer some type of systematic bias from these observations.

To summarize the above discussion, results of the intercomparison indicate that both systematic and episodic bias exists in the measurement of $HCOOH_g$ by the various

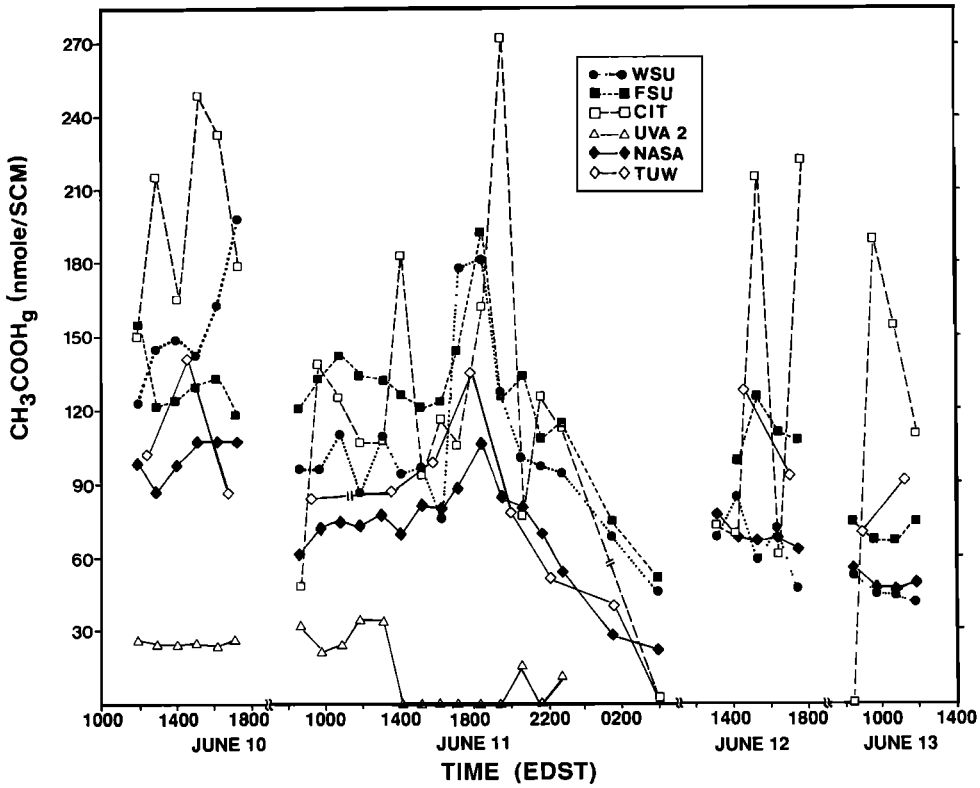

Fig. 3. Concentrations of CH_3COOH_g measured during the intercomparison.

techniques. Based on overall performance, the seven measurement systems can be roughly grouped into three categories. NASA, TUW, and WSU responded similarly to concentration changes and generally detected significantly lower concentrations of $HCOOH_g$ than did UVA 1, FSU, and CIT. Relative to the other six groups, NOAA measured consistently lower concentrations. The nature of some of these artifacts will be assessed in the section on Postintercomparison Experiments.

Acetic acid intercomparison. Five of the seven groups reported data for CH_3COOH_g during the Charlottesville intercomparison. High background levels of CH_3COOH on the GC resins used by UVA 1 limited resolution for quantification of CH_3COOH_g during the 1- to 2-hour sampling

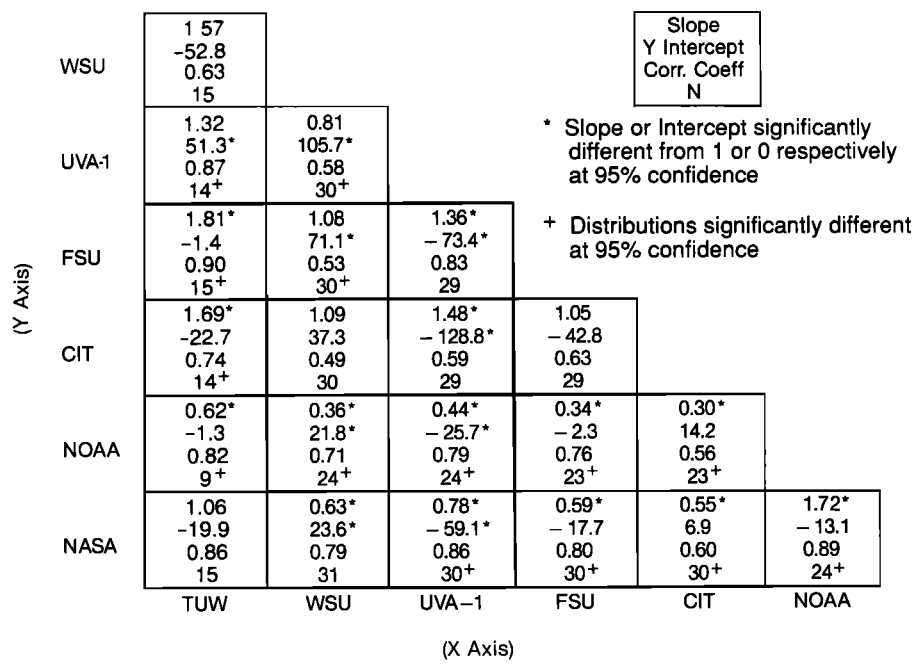

Fig. 4. Matrix of regression parameters and tests of significance for $HCOOH_g$ measured by different systems.

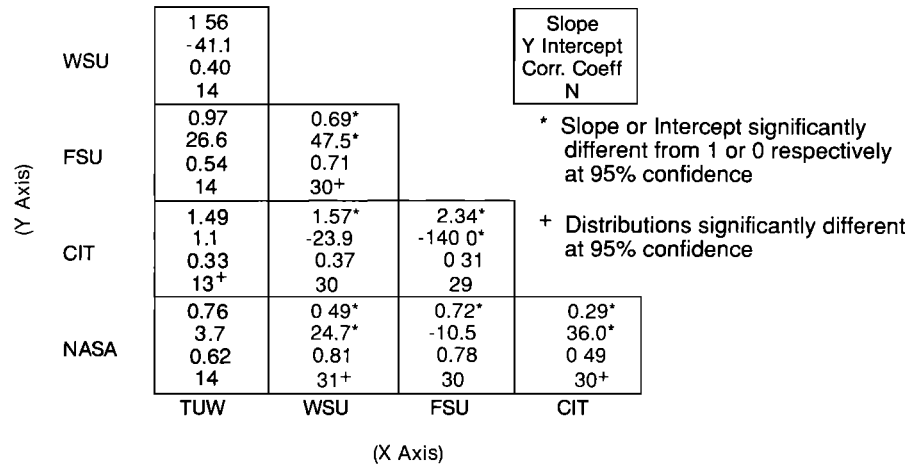

Fig. 5. Matrix of regression parameters and tests of significance for CH_3COOH_g measured by different systems.

intervals, while an analytical problem at the NOAA laboratory prevented verification of the CH_3COOH_g data generated by their measurement system. Like the data for $HCOOH_g$, there was generally poor agreement between the measurements of CH_3COOH_g by participating groups (Figure 3). Hypothesis tests for the median and distribution of all data indicated that at 95% confidence the measurements did not represent random samples from identical populations. Significant bias among the data sets is indicated by these tests.

Results of the hypothesis tests involving the Mann-Whitney technique and the RMA procedure are summarized in Figure 5. There were no significant differences between measurements by NASA and TUW or between those of WSU and TUW, although results for NASA and WSU were significantly different. Distributions for FSU and CIT were statistically indistinguishable, but the slope and intercept were significantly different from 1 and 0, respectively. In general, correlation coefficients for CH_3COOH_g were lower relative to those for $HCOOH_g$ regressions.

Relative variability of formic and acetic acids. Relative variability in the concentrations of $HCOOH_g$ and CH_3COOH_g measured with various techniques (Figure 6) provides additional information with which to assess the observed bias among measurement systems. In general, FSU measured proportionately more $HCOOH_g$ compared to CH_3COOH_g relative to the other four groups. Although the absolute magnitude varies, data for both NASA and FSU suggest a diel cycle in the ratio of the two acids. Similar cycles in the atmospheric concentrations of the gases measured with the NASA mist chamber have also been observed at Hampton, Virginia [*Talbot et al.*, 1988]. Ratios of $HCOOH_g$ to CH_3COOH_g observed by WSU show fairly consistent variability from sample to sample but a clearly discernible diel trend is not evident in the data. These patterns support results of our statistical analysis which indicated that FSU, NASA, and WSU may not be measuring exactly the same atmospheric species. The relatively fewer numbers of measurements by TUW and the greater uncertainties in the CIT data (see previous discussion) limits resolution in assessing trends in ratios of $HCOOH_g$ to CH_3COOH_g measured with those techniques.

Postintercomparison experiments. As described in the Methods section, experiments subsequent to the Charlottesville intercomparison evaluated the performance of the NASA mist chamber and the FSU impregnated filter system under a variety of conditions. Results of these measurements allow us to assess the nature of systematic differences between these techniques, and to speculate about the quality of measurements obtained with the other systems that were intercompared in central Virginia.

Data generated during the Tallahassee intercomparison are summarized in Table 5. Measurements with the impregnated filter and mist chamber techniques of $HCOOH_g$ in a zero air stream agreed within 10% at a concentration of approximately 150 nmol/SCM (Table 5). At a similar concentration, measurements of CH_3COOH_g with the mist chamber technique were approximately 20% higher than were those with the impregnated filter. These differences were small compared to the up to fivefold bias observed for measurements in ambient air during the Charlottesville intercomparison (Figure 2). When the two systems simultaneously sampled carboxylic acids in ambient air at Tallahassee, however, significant bias similar in magnitude to that observed in Charlottesville was detected (Table 5). Studies conducted previously indicate that the mist chamber was not subject to a negative interference [see *Talbot et al.*, 1988]. Taken together, these results suggest that the FSU impregnated filter technique and by inference the methods used by UVA 1 and CIT, may be subject to large positive artifacts when sampling carboxylic acids in tropospheric air.

A final set of measurements was conducted at Tallahassee, to examine the effects of CH_2O_g on the quantification of $HCOOH_g$ and CH_3COOH_g with the FSU impregnated filter method. An elevation in the apparent atmospheric concentrations of both $HCOOH_g$ and CH_3COOH_g was observed in the air stream to which CH_2O was added relative to unaltered ambient air (Table 5). These results indicate that CH_2O may cause a positive interference in the measurement of carboxylic acids using the FSU impregnated filter technique.

Results of the intercomparison experiments conducted at NASA are summarized in Table 6. With the mist chamber technique, no significant differences were found in the concentrations of $HCOOH_g$ and CH_3COOH_g measured in ambient air with and without CH_2O added (Table 6).

As observed in Tallahassee (Table 5), however, results for the FSU impregnated filter sets showed a four to fivefold increase in the concentration of $HCOOH_g$ and CH_3COOH_g

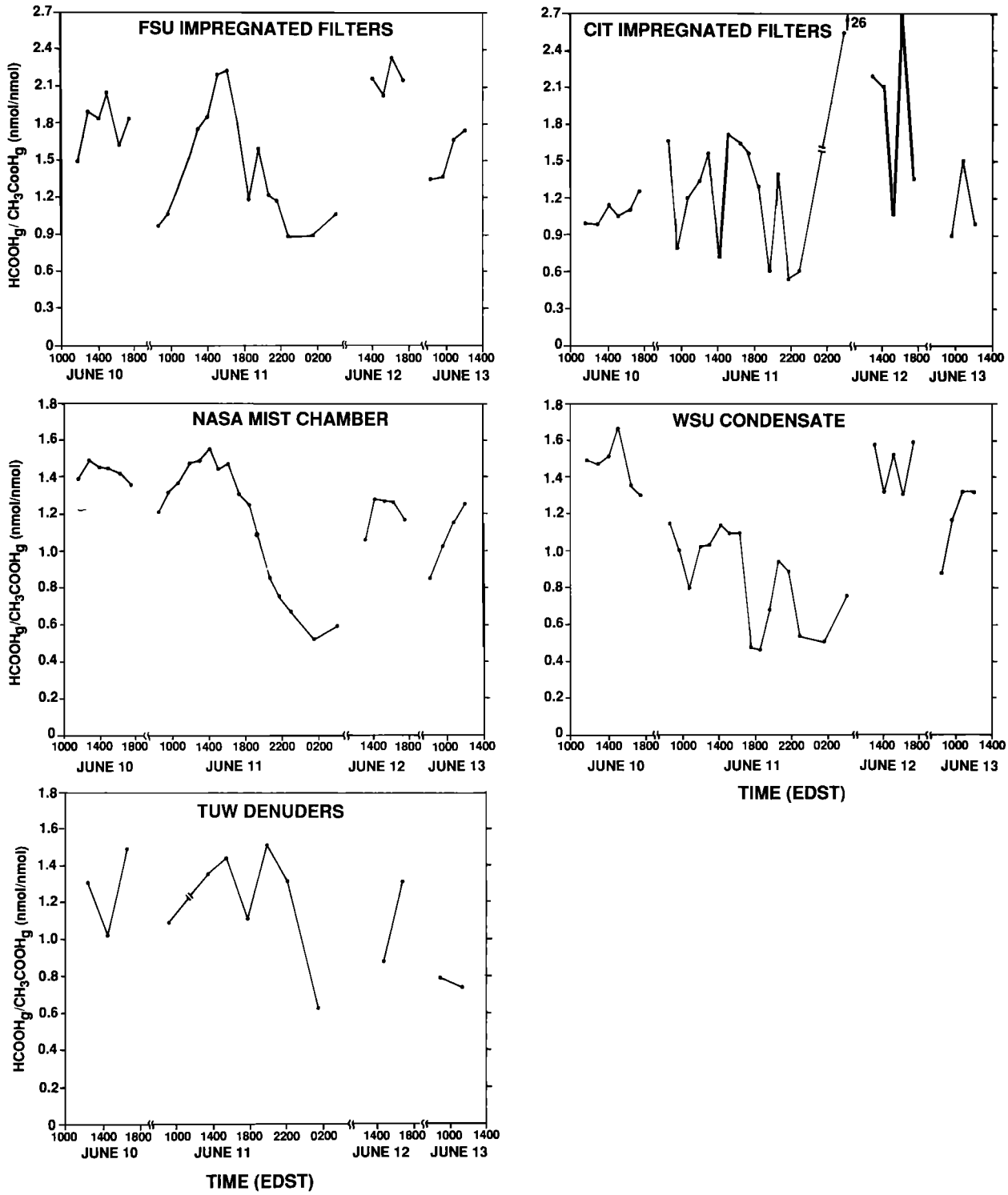

Fig. 6. Ratios of $HCOOH_g$ to CH_3COOH_g measured during the intercomparison.

determined in the air stream with CH_2O added (Table 6). This positive interference occurred on both stages of the filter pack in about equal proportions for both acids. Relative to the mist chamber, measurements of $HCOOH_g$ in unaltered ambient air using the FSU impregnated filter system were a factor of 3 higher, although both techniques detected similar concentrations of CH_3COOH_g. This observation suggests that the interference for the two carboxylic acids may not be directly related.

The fairly extensive experimentation completed to date has identified no significant artifacts in the measurement of $HCOOH_g$ and CH_3COOH_g using the mist chamber technique. The similarity of results obtained during the intercomparison with the TUW denuder sampler and the NASA system suggests that the denuder technique may also be free of significant artifacts. Some caution is, however, warranted when using liquid water mist or condensate to collect gaseous carboxylic acids. As acidic gases are scavenged, the *p*H of the aqueous

TABLE 5. Summary of Results for NASA/FSU Intercomparison Conducted in Tallahassee, Florida, November 3–4, 1986

		$HCOOH_g$, nmol/SCM	CH_3COOH_g, nmol/SCM	$HCOOH_g/CH_3COOH_g$
Permeation Device Intercomparison in Zero Air Stream				
Mist chamber	(N = 6)	143 ± 3	167 ± 4	0.85 ± 0.03
Impregnated filter	(N = 2)	158 ± 2	136 ± 2	1.2 ± 0.03
Ambient Air Intercomparison				
Mist chamber	(1 hour)	27	24	1.1
	(2 hours)	35	32	1.1
Impregnated filter	(1 hour)	110	111	0.99
	(2 hours)	114	65	1.8
Effects of CH_2O Addition on Ambient Air Measurements With the Impregnated Filter				
Ambient air		74	28	2.6
Ambient air plus CH_2O		113	145	0.78

media will typically drop. This can affect the phase partitioning of CH_3COOH which has a relatively high pK_a of 4.76. It is evident that for the mist chamber, long sampling intervals, particularly in regions with high concentrations of soluble acidic gases, may lead to reduced collection efficiencies. Similar problems could affect the condensate technique under conditions of low relative humidity and high concentrations of soluble acidic gases. It is also possible that aqueous phase reactions such as those involving CH_2O, $HCOO^-$, and OH radicals [e.g., *Jacob*, 1986] could lead to positive or negative artifacts in such sampling systems. Investigators are encouraged to independently verify the performance of collection techniques involving aqueous phase media under the ambient condition in which they will be deployed.

The strong base impregnated filter techniques are prone to positive interferences in the measurement of $HCOOH_g$ and CH_3COOH_g. The GC resin technique also appears to suffer from such artifacts. While experimental evidence suggests that atmospheric aldehydes may cause artifact HCOOH and CH_3COOH to be produced on the alkaline filters, the exact nature of the interferences were not investigated. We do not know why the impregnated filter system operated by NOAA detected significantly lower concentrations of $HCOOH_g$ relative to the other measurement systems. We also do not know why the TUW denuder with an alkaline surface coating did not show positive interferences similar to other alkaline collection techniques.

Particulate Phase Species

Significant differences were observed between particulate phase concentrations measured by the UVA 1 hi-vol system, NOAA filter pack, and NASA hi-vol system (Figure 7). These differences may correspond to different storage procedures for filters between collection and analysis (Table 1). Immediately after collection, UVA 1 placed exposed filters in glass vials and froze them in the dark at −4°C for approximately 2 months prior to analysis. NOAA placed exposed filters in polyethylene bags and refrigerated them in the dark for 7 days prior to analysis. NASA placed exposed filters in polyethylene bags and stored them in the dark at room temperature for approximately 1 month prior to analysis. These procedures may have given rise to positive or negative artifacts. The microbial transformation of dissolved $HCOO_T$ ($HCOOH_{aq}$ + $HCOO^-$) and CH_3COO_T (CH_3COOH_{aq} + CH_3COO^-) is well documented for both refrigerated [e.g., *Keene and Galloway*, 1984] and unrefrigerated [*Herlihy et al.*, 1987] samples of precipitation. If such a process occurred on filters, the measurements of NOAA and NASA may have underestimated ambient atmospheric concentrations, resulting in a negative artifact. Alterna-

TABLE 6. Summary of Results for NASA/FSU Intercomparison Conducted in Hampton, Virginia, November 10–11, 1986

	$HCOOH_g$, nmol/SCM	CH_3OOH_g, nmol/SCM	$HCOOH_g/CH_3COOH_g$
Effects of CH_2O Addition on Ambient Air Measurements With the Mist Chamber			
Ambient air	13	12	1.1
Ambient air plus CH_2O	14	12	1.2
Effects of CH_2O Addition on Ambient Air Measurements With the Impregnated Filter			
Ambient air			
filter 1	16	15	1.1
filter 2	2	5	0.40
total	18	20	0.90
Ambient air plus CH_2O			
filter 1	71	51	1.4
filter 2	41	58	1.5
total	112	79	1.4
Ambient air			
mist chamber*	6.5	20	0.33

*Simultaneously measured with impregnated filters.

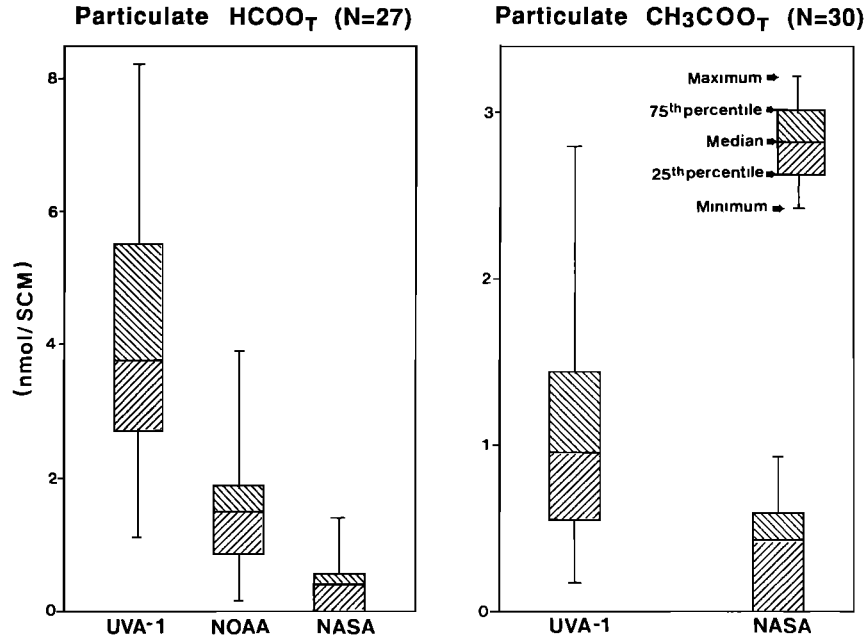

Fig. 7. Distributions for concentrations of particulate $HCOO_T$ and CH_3COO_T measured by the UVA 1 hi-vol, the NOAA filter pack, and the NASA hi-vol systems.

tively, the freezing procedure of UVA 1 may have ruptured natural biogenic aerosols such as pollen which could release $HCOO_T$ and CH_3COO_T resulting in a positive artifact. Differences in extraction procedures may have also contributed to the observed variability. Sonification which was used by UVA 1 and NOAA but not by NASA also could have ruptured biogenic aerosols or facilitate the aqueous phase production of HCOOH and CH_3COOH from decomposition of organic compounds resulting in apparently higher atmospheric concentrations. Additional experimentation is needed to resolve the nature of bias in the measurements of particulate phase carboxylic acids.

The results of the stacked filter pack which was operated by NASA are summarized in Table 7. As previously discussed, the interpretation of these data is complicated by the potential for artifacts. In general, however, higher total concentrations of particulate $HCOO_T$ and CH_3COO_T were measured by NASA using the lo-vol stacked filter pack relative to the hi-vol sampler (Figure 7). Such an effect could be explained by the larger pressure drop across the hi-vol filter resulting in volatilization of vapor from aerosols. Additional experimentation is needed to assess the potential for and magnitude of such an effect.

Results of the storage experiment conducted by NASA subsequent to the Charlottesville intercomparison are summarized in Table 8. For samples which were analyzed immediately after collection, mean variations between filter halves of 17 and 34% for $HCOO_T$ and CH_3COO_T were observed. The frozen samples yielded mean concentrations of $HCOO_T$ and CH_3COO_T which were 56 and 60%, respectively, higher than their refrigerated counterparts. These results suggest that $HCOO_T$ and CH_3COO_T were either lost from the refrigerated samples, most likely via biological degradation, or that the frozen process ruptured aerosol particles releasing additional amounts of carboxylic compounds.

The results of these intercomparisons indicate that procedures for sample collection, storage, and extraction may result in positive or negative artifacts in the measurement of particulate phase concentrations. Unfortunately, because sections of stored filters were not analyzed immediately after collection of particles, definitive information is not available to critically assess the nature of these artifacts. As such, we encourage other investigators to perform carefully designed experiments which will resolve these issues prior to reporting concentration for particulate phase carboxylic species.

TABLE 7. NASA Stacked Filter Pack

			Coarse		Fine		Total	
Date	Time On	Time Off	$HCOO_T$	CH_3COO_T	$HCOO_T$	CH_3COO_T	$HCOO_T$	CH_3COO_T
June 10	1155	1755	1.5	0.44	0.41	0.47	1.9	0.91
June 11	0815	1026	...	...	...	...	...	...
	0951	1254	0.99	0.24	0.49	0.57	1.5	0.81
	1300	1730	0.74	<0.67	0.36	0.62	1.1	0.62
	1806	1838	...	...	...	...	...	...
	1846	2314	0.42	<0.39	0.75	0.98	1.2	0.98
June 12	0000	0500	<0.32	<0.24	0.35	0.86	0.35	0.86
	1251	1751	1.2	0.30	0.54	0.56	1.7	0.86
June 13	0652	1222	1.5	0.44	0.22	<0.82	1.7	0.44

Values are given in nmol/SCM. Coarse, >1.5 μm; fine, <1.5 μm.

TABLE 8. Results of Storage Experiment for Particulate Phase $HCOO_T$ and CH_3COO_T

	Filter 1 Halves		Filter 2 Halves	
	A	B	A	B
	No Storage: Immediate Analysis			
$HCOO_T$	0.15	0.20	0.21	0.23
CH_3COO_T	0.06	0.14	0.18	0.20
	Storage: 20 Days			
$HCOO_T$	0.38	1.1	0.50	0.91
CH_3COO_T	0.14	0.37	0.17	0.42

The filter pairs that were analyzed immediately after collection were not simultaneously collected with those that were stored for 20 days prior to analysis. Storage conditions: A, Sealed in double polyethylene bags and stored at 4°C in the dark; B, placed in a Teflon centrifuge tube, sealed in a polyethylene bag, and stored at −5°C in the dark (frozen). Atmospheric concentrations are given in nmol/SCM. Sampling period was 4 hours. Estimated detection limits are 0.06 nmol/SCM for $HCOO_T$ and 0.04 nmol/SCM for CH_3COO_T.

Until such investigations are carried out, particulate phase data must be viewed with caution and an appreciation of potential limitations.

Intercalibrations of Analytical Techniques

Analytical intercalibrations typically agreed within approximately ±10% or ±1 μmol/L of expected values (Table 9). These differences are small compared to the overall differences between results generated by participating groups. The observed differences between the various techniques appear to originate primarily from the specificity of sampling media, handling, or storage rather than with analytical bias.

Several additional factors not addressed by such an intercalibration should also be considered. The majority of participating groups used standard ion chromatography (IC) to analyze their samples (Table 2). However, IC techniques frequently do not discriminate definitively between lactate ($CH_3CHOHCOO_T$) and CH_3COO_T (K. Rice, Dionex Corporation, personal communication, 1988). $CH_3CHOHCOO_T$ has been observed in atmospheric samples by a number of investigators (see, for example, *Keene et al.* [1983] and *Likens et al.* [1983], among others) and could represent a significant source of bias in some regions. Investigators are encouraged to verify their measurements of CH_3COOH by intercomparing with results generated by a specific analytical technique such as Ion Exclusion Chromatography (ICE).

Peroxyacetyl nitrate (PAN) is also a potential interferent in measurements of CH_3COOH. PAN hydrolyzes to give CH_3COO^- and NO_2^- in alkaline solutions such as the water film on base impregnated filters or the basic eluents used in IC. Although PAN levels were probably low compared to carboxylic acids during the Charlottesville intercomparison, such an artifact could be significant in more polluted environments.

CONCLUSIONS

1. Nylasorb membranes did not retain $HCOOH_g$ or CH_3COOH_g quantitatively. Evidence suggests that other atmospheric constituents either compete for collection sites or react with and destroy $HCOOH_g$ and CH_3COOH_g collected on the membranes.

2. Significant systematic and episodic artifacts exist among many currently deployed measurement systems for $HCOOH_g$ and CH_3COOH_g.

3. Based on previously published data [*Talbot et al.*, 1988] and on results generated during this study, no significant positive or negative interferences were found for the NASA mist chamber technique. Thermodynamic considerations suggest, however, that caution should be exercised when using this and other techniques involving aqueous phase media to collect carboxylic acids.

4. There were no significant differences between results generated by the NASA mist chamber and the TUW denuder collection system, suggesting that the denuder technique is also free of positive or negative interferences in the measurement of $HCOOH_g$ and CH_3COOH_g.

5. Evidence for significant episodic artifacts in the measurement of $HCOOH_g$ was observed between the condensate technique and the mist chamber. Similar, though not significant, differences were observed between results for the condensate technique and the denuder system.

TABLE 9. Intercalibration of Analytical Techniques

	Aliquot 1		Aliquot 2	
Group	$HCOO_T$, μmol/L	CH_3COO_T, μmol/L	$HCOO_T$, μmol/L	CH_3COO_T, μmol/L
WSU	22.7	25.4	1.2	1.27
UVA 1	23.2	25.5	0.65	2.08
FSU	23.8	25.9	1.32	2.30
CIT	22.7	25.3	BLD	BLD
NOAA	27.	NR	1.33	
UVA 2	25.1*	21.1*	0.71	1.66
NASA	24.4	27.1	1.26	2.37
TUW	24.9	24.	BLD	BLD
$\bar{X}$ ± SD	24.2 ± 1.46	24.9 ± 1.91	1.08 ± 0.313	1.94 ± 0.464
Expected concentrations of test solutions	23.1	25.2	1.10	1.68

NR, values not reported; BLD, concentration below detection limit.

*Test solutions diluted into lower analytical range. Reported concentrations reflect proportionately larger uncertainties.

6. Alkaline filter techniques and the GC resin technique are prone to large positive interferences in the measurement of $HCOOH_g$ apparently resulting in part from reactions of aldehydes with the sampling media to generate HCOOH subsequent to collection. Aldehyde additions to ambient air streams also resulted in the generation of artifact CH_3COOH on impregnated filter system operated by FSU.

7. Significant bias was observed for particulate phase measurements by participating groups, and it appeared to arise from differences in sample storage and handling subsequent to collection. Experimental evidence was not available to assess the nature of these artifacts.

8. Analytical bias could account for only a minor fraction (<10%) of the observed differences (up to a factor of 5) between results obtained with the various techniques that were intercompared.

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